



Volume 7 of 13 of Submission

**Study Title**

Waiver Request for Hydrolysis for the Evaluation of Sodium Chlorite/Chlorine  
Dioxide for Use on Field Grown Wheat, Barley and Oats

**Data Requirement**

OPPTS 835.2130 (Hydrolysis as a Function of pH and Temperature)

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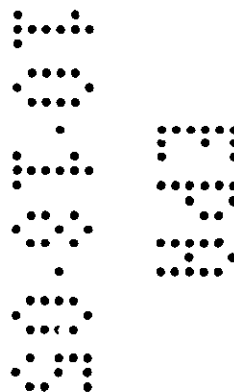
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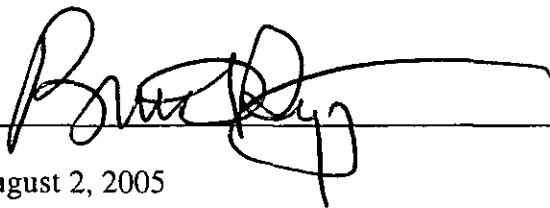
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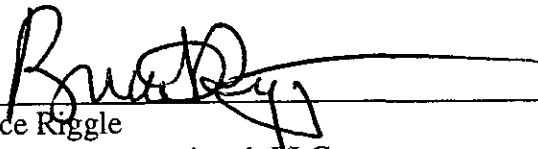
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### Good Laboratory Practices Statement

This review, titled "Waiver Request for Hydrolysis for the Evaluation of Sodium Chlorite /Chlorine Dioxide for Use on Field Grown Wheat, Barley and Oats" is a discussion and presentation of compiled information from published literature. No data are being submitted that are subject to Good Laboratory Standards (40 CFR Part 160).

Submitter:

  
\_\_\_\_\_  
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August 2, 2005

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## INTRODUCTION

In a pre-registration meeting on November 16, 2004, Bi-Oxide Crop Science LLC (Bi-Oxide), requested data waivers for the agronomic food/feed use of sodium chlorite when used on field grown wheat, barley and oats. The U.S. Environmental Protection Agency (EPA) (Agency) Office of Pesticide Programs Registration Division (RD) found this request acceptable since the sodium chlorite/chlorine dioxide chemistry is well known. It was understood in the meeting that acidified sodium chlorite will convert to chlorine dioxide, which in turn will oxidize both organic and inorganic reducing agents and that it is the oxidative mechanism that provides fungicidal activity. It was also understood that the registrant would not be required to generate new data, but instead could submit data waiver requests in the form of literature reviews and could follow the reporting procedure as outlined in PR Notice 86-5. The following outlines what is commonly known about sodium chlorite hydrolysis in water.

## BASIS OF WAIVER REQUEST

As outlined in OPPTS 835.2130 (Hydrolysis as a Function of pH and Temperature), the Agency requires data to determine the potential effects of impurities that could result from hydrolysis and how these impurities could impact the environment. Bi-Oxide requests a waiver from the requirement to submit such data. The active ingredient (sodium chlorite/chlorine dioxide) is a reactive oxidizing material that is eventually reduced to chloride, the terminal residue. Because the terminal residue is chloride, there would be no off-target risk to the environment or humans. Because sodium chlorite and chlorine dioxide are routinely used by some municipalities for water disinfection and because the expected exposure would be low, there should be no harm to the environment, including non-target aquatic and terrestrial plants or animals as well as persons and/or livestock. The following addresses these points in detail for justification of a waiver from the requirement of data.

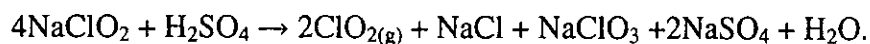
## CHEMISTRY BACKGROUND

The formulated product will be an ionic solution that contains 25% sodium chlorite. Prior to application, the formulation will be diluted in water and an acid will be added. When using an acid, the theoretical conversion of sodium chlorite to chlorine dioxide is 80% (Vulcan, 1998).

In the presence of a mono-valent acid, such as hydrochloric acid, the following reaction is expected to occur:



In the presence of a multi-valent acid, such as sulfuric acid, the following reaction is expected to occur:



It has been reported that in these reactions, typically from 50% to 70% of the reacted  $\text{ClO}_2$  appears as  $\text{ClO}_2^-$  with the balance forming either  $\text{Cl}^-$  (chloride) or  $\text{ClO}_3^-$  (chlorate) (Ellenberger, 1999).

In pure water, sodium chlorite and chlorine dioxide would co-exist in an equilibrium state. In the presence of phenolics, amines and organic sulfides, as well as inorganic iron and manganese, chlorine dioxide would oxidize these materials and in turn would be reduced to chloride. Chlorite would also function as an oxidizing agent and would be reduced to chloride, but at a much slower rate than that of chlorine dioxide (Ellenberger, 1999).

## **PROPOSED USE PATTERN**

Prior to field application, an approved acid will be added (for activation purposes) to the sodium chlorite product (25% ai.) and water. The proposed seasonal use pattern is one (1) application at 0.16 lb ai / acre or two (2) applications at 0.1 lb ai/acre each, the second application following the first by 1 to 3 weeks, depending upon disease pressure. The single or first application would be made to field grown wheat, barley and oats at the flowering (spike) stage.

Application(s) will be made by either aircraft or ground operated equipment. Because the application(s) will be made at heading and due to typical heavy plant populations, the majority of applications would be by aircraft. Aerial applications will use a minimum of 5 gallons of water per acre and ground applications will use between 10 to 20 gallons. Because of the potential corrosive nature of the active ingredient and the acid, the label will prohibit applications through irrigation systems (chemigation).

## **CURRENT USE PATTERN FOR WATER TREATMENT**

Chlorine dioxide is currently used for water treatment. Ellenberger reported that in the United States over 500 water treatment plants use chlorine dioxide full time and as many as 900 use it either part time or seasonally as both a disinfectant for drinking water and for taste and odor control. In its National Primary Drinking Water Regulations, EPA established a maximum contaminate level of 1.0 and 0.8 mg/L (ppm) for chlorite and chlorine dioxide, respectively. By allowing this use and setting allowable residue limits, EPA evaluated the potential for the formation of hydrolysis by-products that could have an adverse impact on drinking water.

## **HYDROLYSIS ASSESSMENT**

Hydrolysis is defined in OPPTS 835.2130 as the chemical reaction of an organic chemical with water such that one or more bonds (of the chemical) are broken and the reaction products incorporate the elements of water ( $\text{H}_2\text{O}$ ). Sodium chlorite ( $\text{NaClO}_2$ ) and chlorine dioxide ( $\text{ClO}_2$ ) do not meet the basic definition as set in OPPTS 835.2130 since neither contains carbon and both are by definition inorganic chemicals. Neither chemical will hydrolyze. In its Guidance Manual for Alternative Disinfectants and Oxidants (April 1999), EPA stated that "Chlorine dioxide in water does not hydrolyze to any appreciable extent but remains in solution as a dissolved gas". The Department of Health and Human Services in its Profile for Chlorine

Dioxide stated that "Chlorine dioxide alone will not hydrolyze in solution to any appreciable extent between pH 2 and 10" and "In the absence of oxidizable substances and in the presence of hydroxyl ions, chlorine dioxide will dissolve in water and then decompose with the slow formation of chlorite and chlorate ions (e.g.,  $2\text{ClO}_2 + 2\text{OH}^- \rightarrow \text{ClO}_2^- + \text{ClO}_3 + \text{H}_2\text{O}$ ). The terminal residue for both chlorite and chlorine dioxide is chloride.

## CONCLUSIONS

Chlorine dioxide and sodium chlorite will not hydrolyze in water and both will remain in solution as either a dissolved gas or an anion. There are no hydrolysis by-products. The terminal residue for both chlorite and chlorine dioxide is chloride.

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Ellenberger, C.S., Thesis: Water Quality Impacts of Pure Chlorine Dioxide Pretreatment at The Roanoke County (Virginia) Water Treatment Plant. Virginia Polytechnic Institute and State University. December 7, 1999. 81 pages.

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Toxicological Profile for Chlorine Dioxide and Chlorite. U.S. Department of Health and Human Services. Public Health Service. Agency for Toxic Substances and Disease Registry. September 2004. page 90 and 92.

U.S. Environmental Agency, List of Drinking Water Contaminates & MCLs

Vulcan Chemicals. Technical Data Sheet. Technical & Environmental Services. TDS 600-103. December 1998.

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**WATER QUALITY IMPACTS OF  
PURE CHLORINE DIOXIDE PRETREATMENT  
AT  
THE ROANOKE COUNTY (VIRGINIA) WATER TREATMENT PLANT**

by  
Christine Spada Ellenberger

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ENVIRONMENTAL ENGINEERING**

Dr. Robert C. Hoehn, Chairman

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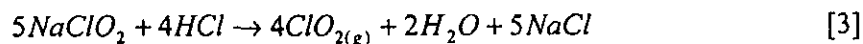
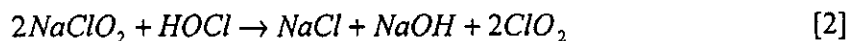
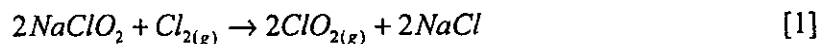
## CHAPTER II LITERATURE REVIEW

### Chlorine Dioxide and By-product Chemistry

Chlorine dioxide ( $\text{ClO}_2$ ) exists as a volatile, energetic free radical and is quite reactive. It is explosive at 5.8 psi (40 kPa), or above atmospheric pressure at 6 psig (41 kPa). As a result,  $\text{ClO}_2$  cannot be compressed or stored and must be generated on-site and solutions with concentrations greater than 10 g/L may present an explosive hazard (Aieta and Berg, 1986). Chlorine dioxide concentrations are generally in the range of 0.1 mg/L to 5.0 mg/L for water treatment.

Chlorine dioxide does not hydrolyze in water but remains a highly soluble gas above 11°C over a broad range of pH (2 to 10). Solutions are greenish-yellow and smell strongly chlorinous (Gordon and Rosenblatt, 1996). Aqueous solutions must be protected from light, as chlorine dioxide is subject to photolysis by ultraviolet light (Zika, 1985), and even fluorescent lights (Griese et al., 1992).

The most common methods for the generation of  $\text{ClO}_2$  for drinking water treatment involve sodium chlorite ( $\text{NaClO}_2$ ), either as a solid or in solution (Aieta and Berg, 1986). Sodium chlorite is reacted with either chlorine gas ( $\text{Cl}_2$ ), hypochlorous acid ( $\text{HOCl}$ ), or hydrochloric acid ( $\text{HCl}$ ) in the following reactions (Aieta and Berg, 1986; Gordon et al., 1972):



During the first two reactions, an unstable intermediate,  $\text{Cl}_2\text{O}_2$ , is formed if the reactants are in high concentrations. When chlorite ion ( $\text{ClO}_2^-$ ) concentrations are low, the intermediate decays to chlorate ion ( $\text{ClO}_3^-$ ). Chlorate ion production can also occur when initial reactant concentrations are low or when chlorine (or hypochlorous acid) is in excess. When initial reactant concentrations are high or when  $\text{ClO}_2^-$  concentrations are in excess, the intermediate decays to  $\text{ClO}_2$  (Gordon and Rosenblatt, 1996).

During the generation of  $\text{ClO}_2$ , it is desirable to minimize or eliminate unwanted by-products such as  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  as well as excess chlorine. The production of unwanted by-products can occur when there is feedstock contamination, improper generator control, or excess chlorine (Long et al., 1996; Gates, 1998). In Reaction 3, only an 80 percent conversion of  $\text{NaClO}_2$  to  $\text{ClO}_2$  is possible (Aieta and Berg, 1986), and, therefore, this method is not popular.

Recently, a method for generating high-purity  $\text{ClO}_2$  by reaction of solid  $\text{NaClO}_2$  with chlorine gas has become available (Gordon and Rosenblatt, 1996). The chlorine gas is first mixed with humidified air and then passed through a series of drums containing solid  $\text{NaClO}_2$ . No unreacted  $\text{NaClO}_2$  enters the system because the generated  $\text{ClO}_2$  is in the gas phase, and  $\text{ClO}_3^-$  is not produced.

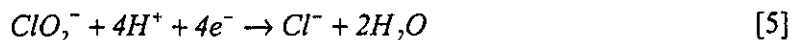
The main reaction product of  $\text{ClO}_2$  in water is the chlorite ion. Its reduction occurs by an one electron transfer, forming  $\text{ClO}_2^-$  as shown in this half-reaction (White, 1972; Gordon et al., 1972):



Masschelein (1979) reported, "In aqueous solution, chlorination by chlorine dioxide is not a direct reaction. However, indirect chlorination by dioxide having undergone a previous

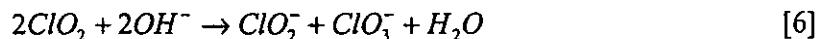
reaction may not necessary be excluded." He attributed reports of chlorinated organic by-products produced to the presence of chlorine in the  $\text{ClO}_2$  solution that was used. Chlorine, on the other hand, reacts with organic compounds to form chlorinated organic by-products (Rook, 1974; Bellar et al., 1974).

Chlorite ion, which also is an oxidant, reacts at a much slower rate than  $\text{ClO}_2$  under conditions generally encountered in water treatment. Chlorite ion is reduced to chloride ion ( $\text{Cl}^-$ ) by the following reaction (Aieta and Berg, 1986; Gordon et al., 1972; Masschelein, 1979):

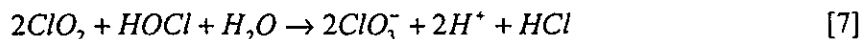


This reaction does not occur, however, unless reduced compounds such as ferrous iron ( $\text{Fe}^{2+}$ ), phenol, or humic materials are present. Typically, from 50 to 70 percent of the reacted  $\text{ClO}_2$  appears as  $\text{ClO}_2^-$  with the balance forming either  $\text{Cl}^-$  or  $\text{ClO}_3^-$  (Aieta and Berg, 1986; Limoni et al., 1984; Rav-Acha et al., 1984; Werdehoff and Singer, 1987; Singer and O'Neil, 1987).

In basic solutions,  $\text{ClO}_2$  disproportionates to form  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  (Aieta and Berg, 1986):



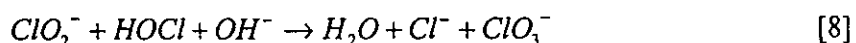
Under certain conditions chlorine and  $\text{ClO}_2$  can react to form  $\text{ClO}_3^-$  (Aieta and Berg, 1986):



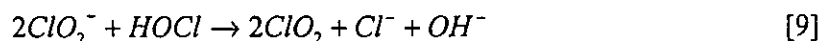
Chlorine dioxide is subject to photochemical decomposition through a series of reactions to  $\text{Cl}^-$  and  $\text{ClO}_3^-$  (Zika, 1985). Griesse et al. (1992) reported significant formation of  $\text{ClO}_3^-$  (0.36 to 0.97 mg/L) when water containing from 3.56 mg/L to 3.99 mg/L  $\text{ClO}_2$  was

exposed to fluorescent light. In control experiments, water treated with  $\text{ClO}_2$  and kept in the dark did not contain  $\text{ClO}_3^-$ .

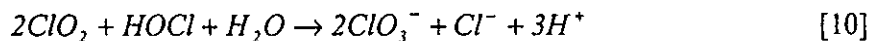
Chlorite ion reacts with chlorine in treated water to reform  $\text{ClO}_2$ , in the same manner that  $\text{ClO}_2$  is generated (Reaction 2 presented previously). This reaction, however, depends heavily on pH and relative reactant concentrations. In basic solutions when the hypochlorite ion ( $\text{OCl}^-$ ) is present, greater amounts of  $\text{ClO}_3^-$  are formed by the following reaction (Gordon et al., 1990; Werdehoff and Singer, 1987):



In acidic solutions when  $\text{ClO}_2^-$  is in excess, more  $\text{ClO}_2$  than  $\text{ClO}_3^-$  is formed (Gordon et al., 1972; Gordon et al., 1990; Werdehoff and Singer, 1987):



In neutral solutions chlorine and  $\text{ClO}_2$  react to form  $\text{ClO}_3^-$  and  $\text{Cl}^-$  (Gordon et al., 1972):



### Chlorine Dioxide Applications in Water Treatment

Chlorine dioxide is commonly used as a preoxidant and primary disinfectant during drinking water treatment. As a preoxidant, it is used mainly as an alternative to chlorine, for trihalomethane (THM) control (Dietrich et al., 1992b). It is also used for taste-and-odor control, manganese and iron oxidation, and color removal. In the United States, over 500 water treatment plants use  $\text{ClO}_2$  full time and as many as 900 use it either part time or seasonally (Hoehn, 1993). In some European countries,  $\text{ClO}_2$  is also used to maintain a distribution system residual. In the United States,  $\text{ClO}_2$  application is generally followed by

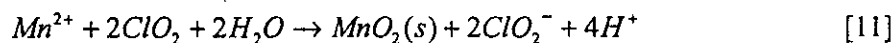


ClO<sub>2</sub> (1.5 mg/L for 120 minutes) followed by monochloramine (2.8 mg/L for 180 minutes) resulted in a 2.8 log-unit (99.84 percent) reduction in infectivity. The expected inactivations by ClO<sub>2</sub>, free chlorine or monochloramine alone were 1.7 (98 percent), 0.0, and 0.0 log-units, respectively. The researchers hypothesized that the synergistic effect demonstrated by sequential disinfection is because "the stronger oxidant conditions the outer membrane of the oocysts so that the secondary oxidant can penetrate the oocyst wall more readily."

### Manganese Oxidation

Soluble manganese (Mn<sup>2+</sup>), which is commonly found in groundwater sources and reservoirs, can cause staining of laundry and plumbing fixtures, and black water (White, 1972). A secondary maximum contaminant level (MCL) of 0.05 mg Mn/L has been set for manganese to avoid these problems (Federal Register, 1979). During water treatment, Mn<sup>2+</sup> is typically removed by oxidation and the resulting precipitate, manganese dioxide (MnO<sub>2</sub>), is then removed by sedimentation and/or filtration (Knocke et al., 1987). Chlorine dioxide has been shown to be an effective manganese oxidant and reacts more rapidly than chlorine (White, 1972).

The oxidation-reduction reaction between Mn<sup>2+</sup> and ClO<sub>2</sub> yields ClO<sub>2</sub><sup>-</sup>, which involves a one-electron transfer between ClO<sub>2</sub> and ClO<sub>2</sub><sup>-</sup>. Experiments conducted by Knocke et al. (1990) demonstrated that ClO<sub>2</sub><sup>-</sup> cannot oxidize Mn(II). The reaction between ClO<sub>2</sub> and Mn<sup>2+</sup> at a neutral pH occurs as follow (Knocke et al., 1990):

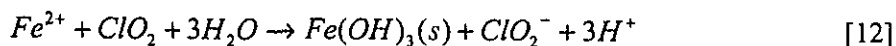


From the stoichiometry, 2.45 mg of chlorine dioxide are required to oxidize 1 mg of soluble manganese (White, 1972). Knocke et al. (1987) reported that a ClO<sub>2</sub> dose at least

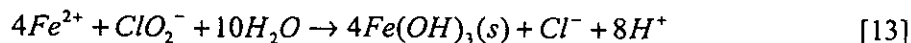
twice the stoichiometric quantity was required to reduce manganese levels below the secondary MCL (0.05 mg Mn/L). In that study,  $\text{ClO}_2$  was effective over a pH range of 5 to 8 and at temperatures as low as 50°F (10°C). Chlorine dioxide dosages greater than 3 mg/L were required to reduce manganese concentrations to less than 0.05 mg Mn/L, when the total organic carbon (TOC) concentration was 8 mg/L. In water treatment applications,  $\text{ClO}_2$  dosages of this magnitude would not be practical unless the resulting  $\text{ClO}_2^-$  concentration was reduced to below the MCL by the addition of ferrous iron or reduced-sulfur compounds. Knocke et al. (1990) showed that manganese forms a weak complex with organic acids and is capable of being oxidized by  $\text{ClO}_2$ .

### Iron Oxidation

Iron can also cause staining of laundry and plumbing fixtures and promote the growth of iron bacteria in the distribution system (White, 1972). A secondary MCL of 0.3 mg/L has been set for iron to avoid these problems (Federal Register, 1979). Chlorine dioxide can rapidly oxidize iron to an insoluble, iron hydroxide ( $\text{Fe}(\text{OH})_3$ ), which can be removed by sedimentation and filtration. Iron oxidation by  $\text{ClO}_2$  under water treatment conditions, occurs as follows (Knocke et al., 1990):



From the stoichiometry, 1.2 mg of chlorine dioxide was required to oxidize 1 mg of soluble iron (White, 1972). Chlorite ion also can oxidize Fe(II); the reaction is summarized as follows (Ondrus and Gordon, 1972):



Chlorine dioxide also can oxidize iron when it is complexed with organic compounds (Masschelein, 1979). Knocke et al. (1990), however, found that Fe(II) complexed with organics was stable in the presence of  $\text{ClO}_2$ , even when the  $\text{ClO}_2$  dosage was well in excess of the stoichiometric amount.

### **Analytical Techniques**

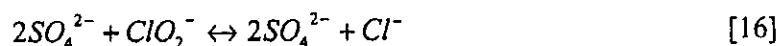
Several methods for quantifying  $\text{ClO}_2$ ,  $\text{ClO}_2^-$ , and  $\text{ClO}_3^-$  are available. These include amperometric titration, N, N-diethyl-p-phenylenediamine titration (DPD), iodometric titration, chlorophenol red, and ion chromatography. The amperometric method is approved for compliance monitoring of  $\text{ClO}_2$ , and ion chromatography is approved for  $\text{ClO}_2^-$  analyses (Federal Register, 1998). The lissamine green B Method for detection of  $\text{ClO}_2$  at low levels in the presence of chlorine, has been developed, but it is not currently an EPA-approved method. These methods are discussed in the following sections.

### **The Amperometric Method**

The amperometric method can be used to determine  $\text{ClO}_2$ ,  $\text{Cl}_2$ ,  $\text{ClO}_2^-$ , and  $\text{ClO}_3^-$ . It involves titrimetric determination of iodine that is formed when iodide is oxidized by the species of interest by titration. The titrant may be either phenylarsine oxide (PAO) or sodium thiosulfate (Aieta et al., 1984; APHA, 1995). During the procedure, several titration steps are required following various pretreatment and pH adjustments that allow differentiation between the various species. According to Aieta et al. (1984), "calculations are based on the equivalents of reducing titrant required to react with the equivalents of oxidants present." No differentiation is made between free and combined chlorine by this procedure.

### Reduction by Reduced-Sulfur Compounds

Gordon et al. (1990) reported  $\text{ClO}_2^-$  reduction by sulfur dioxide-sulfite ion ( $\text{SO}_2\text{-SO}_3^{2-}$ ), which they said occurred by the following reaction over a pH range of 4.0 to 7.5:



Their research indicated that  $\text{ClO}_2^-$  removal was more rapid when the pH was acidic. The authors reported complete  $\text{ClO}_2^-$  reduction in less than one minute when a tenfold weight excess of sulfur dioxide/sulfite ( $\text{SO}_2\text{-SO}_3^{2-}$ ) was reacted with 0.5 to 7.0 mg/L  $\text{ClO}_2^-$  at pH 5 and below and complete  $\text{ClO}_2^-$  reduction in less than 15 minutes at pH 6.5. The authors noted that dissolved oxygen may interfere with  $\text{SO}_2\text{-SO}_3^{2-}/\text{ClO}_2^-$  reaction by competing for  $\text{SO}_2\text{-SO}_3^{2-}$ .

Griese et al. (1991) achieved complete  $\text{ClO}_2^-$  reduction following the addition of  $\text{SO}_2\text{-SO}_3^{2-}$ , but significant amounts of  $\text{ClO}_3^-$  were formed when the pH ranged from 4.0 to 8.5. The authors noted an increase in  $\text{ClO}_3^-$  concentration when the  $\text{SO}_2\text{-SO}_3^{2-}/\text{ClO}_2^-$  reaction occurred in the presence of dissolved oxygen. These results concur with those of Dixon and Lee (1991), who also noted significant  $\text{ClO}_3^-$  formation. Griese et al. (1991) concluded that the application of sulfur-based reducing agents was not a viable strategy for  $\text{ClO}_2^-$  removal during drinking water treatment. Griese et al. (1991) also evaluated sodium thiosulfate for  $\text{ClO}_2^-$  removal and found that it effectively reduced  $\text{ClO}_2^-$  over a pH range of 4.5 to 6.5, but the reaction was heavily dependent on pH and contact time. No significant  $\text{ClO}_3^-$  was formed.

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April 1999, page 4-1.

In drinking water, chlorite ( $\text{ClO}_2^-$ ) is the predominant reaction endproduct, with approximately 50 to 70 percent of the chlorine dioxide converted to chlorite and 30 percent to chlorate ( $\text{ClO}_3^-$ ) and chloride ( $\text{Cl}^-$ ) (Werdehoff and Singer, 1987).

## 4.2 Generation

### 4.2.1 Introduction

One of the most important physical properties of chlorine dioxide is its high solubility in water, particularly in chilled water. In contrast to the hydrolysis of chlorine gas in water, chlorine dioxide in water does not hydrolyze to any appreciable extent but remains in solution as a dissolved gas (Aieta and Berg, 1986). It is approximately 10 times more soluble than chlorine (above  $11^\circ\text{C}$ ), while it is extremely volatile and can be easily removed from dilute aqueous solutions with minimal aeration or recarbonation with carbon dioxide (e.g. softening plants). Above  $11$  to  $12^\circ\text{C}$ , the free radical is found in gaseous form. This characteristic may affect chlorine dioxide's effectiveness when batching solutions and plumbing appropriate injection points. Other concerns are the increased difficulty in analyzing for specific compounds in the presence of many interfering compounds/residual longevity and volatility of gaseous compounds. In the gaseous form, the free radicals also react slowly with water. The reaction rate is 7 to 10 million times slower than that of the hydrolysis rate for chlorine gas (Gates, 1989).

Chlorine dioxide cannot be compressed or stored commercially as a gas because it is explosive under pressure. Therefore, it is never shipped. Chlorine dioxide is considered explosive at higher concentrations which exceed 10 percent by volume in air, and its ignition temperature is about  $130^\circ\text{C}$  ( $266^\circ\text{F}$ ) at partial pressures (National Safety Council Data Sheet 525 –  $\text{ClO}_2$ , 1967). Strong aqueous solutions of chlorine dioxide will release gaseous chlorine dioxide into a closed atmosphere above the solution at levels that may exceed critical concentrations. Some newer generators produce a continuous supply of dilute gaseous chlorine dioxide in the range of 100 to 300 mm-Hg (abs) rather than in an aqueous solution (National Safety Council, 1997). For potable water treatment processes, aqueous solutions between 0.1 and 0.5 percent are common from a number of current generation technologies.

Most commercial generators use sodium chlorite ( $\text{NaClO}_2$ ) as the common precursor feedstock chemical to generate chlorine dioxide for drinking water application. Recently, production of chlorine dioxide from sodium chlorate ( $\text{NaClO}_3$ ) has been introduced as a generation method where in  $\text{NaClO}_3$  is reduced by a mixture of concentrated hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Chlorate-based systems have traditionally been used in pulp and paper applications, but have recently been tested full-scale at two U.S. municipal water treatment plants. This is an emerging technology in the drinking water field and is not discussed in this guidance manual.

## Reference

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**TOXICOLOGICAL PROFILE FOR  
CHLORINE DIOXIDE AND CHLORITE**

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Public Health Service  
Agency for Toxic Substances and Disease Registry

September 2004

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## 6. POTENTIAL FOR HUMAN EXPOSURE

Rahman (1985) reported that the presence of  $\text{ClO}_2$  and  $\text{HOCl}$  ( $\text{Cl}_2$  dissolved in water) inhibit the formation of trihalomethanes, and the degree of inhibition depends on the ratio of  $\text{ClO}_2$  to  $\text{HOCl}$ .

**6.3.2.1 Air**

Chlorine dioxide gas is unstable and can rapidly decompose at high concentrations ( $>40$  kPa partial pressure). It also decomposes to chlorine and oxygen with exposure to mild heat, noise, flame, and a minor pressure wave at low concentrations (Dobson and Cary 2002). Chlorine dioxide will decompose upon exposure to sunlight (Vogt et al. 1986). The gas-phase absorption spectrum for chlorine dioxide is the same as in aqueous solution (Kaczur and Cawfield 1993). The primary photochemical reaction of  $\text{ClO}_2$  in the gas phase corresponds to homolytic scission of one of the chlorine-oxygen bonds (i.e.,  $\text{ClO}_2 \rightarrow \text{ClO} + \text{O}$ ). Products of this initial reaction generate secondary products including doublet-state oxygen ( $\text{O}_2^*$ ), chlorine ( $\text{Cl}_2$ ), and chlorine trioxide ( $\text{Cl}_2\text{O}_3$ ) (Griese et al. 1992; Zika et al. 1984). If chlorine dioxide gas is diluted in air to  $<15$  volume percent, it can be relatively stable in darkness (Vogt et al. 1986).

**6.3.2.2 Water**

Chlorine dioxide is readily soluble in water, forming a greenish-yellow solution. It is not unusual to simultaneously have multiple chlorine species present in chlorine dioxide solutions originating from by-products or unreacted precursors. Table 6-2 lists the various chlorine species that might be present in solutions of chlorine dioxide (Gordon 2001).

Chlorine dioxide alone will not hydrolyze in solution to any appreciable extent between pH 2 and 10. Dilute neutral or acidic aqueous solutions of chlorine dioxide are stable if kept cool, well sealed, and protected from sunlight. In the absence of oxidizable substances and in the presence of hydroxyl ions, chlorine dioxide will dissolve in water and then decompose with the slow formation of chlorite and chlorate ions (e.g.,  $2\text{ClO}_2 + 2\text{OH}^- \rightarrow \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O}$ ). At chlorine dioxide concentrations in the 5–10 mg/L range at pH 12, the decomposition half-life of chlorine dioxide in solution ranges from 20 to 180 minutes (Aieta and Berg 1986; Stevens 1982; WHO 2000). Lee et al. (2004) found that the concentration of chlorate ions formed from chlorine dioxide were higher at low pHs. For example,



## 6. POTENTIAL FOR HUMAN EXPOSURE

10 and 15% chlorate ions were formed from chlorine dioxide at pHs 4 and 7, respectively. At pH 10, chlorate ions were not formed at all.

Chlorine dioxide has a positive chlorine-oxidation state of four (+4), which is intermediate between chlorite (+3) and chlorate (+5) ions. Reduction of chlorine dioxide usually results in the formation of chlorite ions (e.g.,  $\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$ ;  $E^{\text{pH}=7}=0.95$  volts). Chlorite ions ( $\text{ClO}_2^-$ ) are also effective oxidizing agents, although they react much slower than chlorine dioxide. The reduction of chlorite results in the formation of chloride ions (e.g.,  $\text{ClO}_2^- + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$ ;  $E^{\text{pH}=7}=0.37$  volts). The redox potential at pH 7 (i.e.,  $E^{\text{pH}=7}$ ) indicates that chlorine dioxide is a stronger oxidizer than chlorite ions (Rav-Acha 1998). During water-treatment, approximately 50–70% of the chlorine dioxide reacted will immediately appear as chlorite and chloride (Aieta and Berg 1986; Stevens 1982).

Chlorine dioxide, like other strong oxidants, will oxidize manganese (II), iron (II), iodide ( $\text{I}^-$ ), and sulfide ( $\text{S}^{2-}$ ), forming insoluble manganese dioxide ( $\text{MnO}_2$ ), iron hydroxides precipitates, iodine ( $\text{I}_2$ ), and sulfate ( $\text{SO}_4^{2-}$ ), respectively (Dernat and Pouillot 1992). In the absence of sunlight, bromide ( $\text{Br}^-$ ) is not oxidized by chlorine dioxide. Thus, chlorine dioxide will not transform bromide into hypobromite ( $\text{OBr}^-$ ), which could react with organic matter to form bromoform ( $\text{CHBr}_3$ ) or bromate ( $\text{BrO}_3^-$ ). This is a significant difference between the use of chlorine dioxide as an oxidant and the use of chlorine or ozone as oxidants in water-treatment systems (Aieta and Berg 1986; Stevens 1982; WHO 2000).

Since chlorine dioxide reacts generally as an electron acceptor, hydrogen atoms present in activated organic CH or NH bonds do not react by electrophilic substitution with chlorine (Hoigne and Bader 1994). As a result, chlorine dioxide will form fewer chlorinated compounds compared to  $\text{Cl}_2$  when it reacts with organic matter. In contrast, chlorine ( $\text{Cl}_2$ ) reacts not only by oxidation, but also by electrophilic substitution, resulting in a variety of volatile and nonvolatile chlorinated organic products; for example, trihalomethanes (THMs). It has been well established that “chlorine-free” chlorine dioxide in reaction with both humic and fulvic acids does not form THMs. However, some other types of chlorinated organics may be formed from the reaction of chlorine dioxide with humic and fulvic acids (Aieta and Berg 1986; Stevens 1982). The reactions of chlorine dioxide with olefin compounds in wastewater are apparently very complex and produce a host of chlorinated and nonchlorinated products. No evidence exists that chlorine dioxide undergoes reactions with saturated aliphatic hydrocarbons under mild conditions. Chlorine dioxide does not seem to cause the formation of odorous compounds with phenol. Chlorine dioxide treatment of phenols can cause chlorine substitution, ring cleavage, or both, depending on the particular phenol reacted and the conditions of the reaction. Through complex

## **Reference**

U.S. Environmental Agency, List of Drinking Water Contaminates & MCLs

## U.S. Environmental Protection Agency

### List of Drinking Water Contaminates & MCLs

#### National Primary Drinking Water Regulations

National Primary Drinking Water Regulations (NPDWRs or primary standards) are legally enforceable standards that apply to public water systems. Primary standards protect public health by limiting the levels of contaminants in drinking water. Visit the list of regulated contaminants with links for more details.

#### Disinfection Byproducts

| Contaminant                          | MCLG (mg/L)      | MCL or TT (mg/L) | Potential Health Effects from Ingestion of Water                    | Sources of Contaminant in Drinking Water |
|--------------------------------------|------------------|------------------|---|--|
| <u>Bromate</u>                       | zero             | 0.010            | Increased risk of cancer  | Byproduct of drinking water disinfection |
| <u>Chlorate</u>                      | 0.13             | 1.0              | Anemia; infants & young children: nervous system effects            | Byproduct of drinking water disinfection |
| <u>Haloacetic acids (HAA5)</u>       | n/a <sup>6</sup> | 0.060            | Increased risk of cancer  | Byproduct of drinking water disinfection |
| <u>Total trihalomethanes (TTHMs)</u> | none             | 0.10             | Liver; kidney of certain fish; volts system; irritation of the eyes | Byproduct of drinking water disinfection |
| <u>Trihalomethanes (THMs)</u>        | n/a <sup>6</sup> | 0.080            | Increased risk of cancer  | Byproduct of drinking water disinfection |

#### Disinfectants

| Contaminant                                  | MRDLG (mg/L)           | MRDL (mg/L)           | Potential Health Effects from Ingestion of Water         | Sources of Contaminant in Drinking Water |
|--|------------------------|-----------------------|--|--|
| <u>Chloramines (as Cl<sub>2</sub>)</u>       | MRDLG=4 <sup>1</sup>   | MRDL=4.0 <sup>1</sup> | Eye/nose irritation; stomach discomfort, anemia          | Water additive used to control microbes  |
| <u>Chlorine (as Cl<sub>2</sub>)</u>          | MRDLG=4 <sup>1</sup>   | MRDL=4.0 <sup>1</sup> | Liver; irritation of the eyes; irritation of the skin    | Water additive used to control microbes  |
| <u>Chlorine dioxide (as ClO<sub>2</sub>)</u> | MRDLG=0.8 <sup>1</sup> | MRDL=0.8 <sup>1</sup> | Anemia; infants & young children: nervous system effects | Water additive used to control microbes  |

## Notes

<sup>1</sup> Definitions:

**Maximum Contaminant Level (MCL)** - The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.

**Maximum Contaminant Level Goal (MCLG)** - The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals.

**Maximum Residual Disinfectant Level (MRDL)** - The highest level of a disinfectant allowed in drinking water. There is convincing evidence that addition of a disinfectant is necessary for control of microbial contaminants.

**Maximum Residual Disinfectant Level Goal (MRDLG)** - The level of a drinking water disinfectant below which there is no known or expected risk to health. MRDLGs do not reflect the benefits of the use of disinfectants to control microbial contaminants.

**Treatment Technique** - A required process intended to reduce the level of a contaminant in drinking water.

<sup>2</sup> Units are in milligrams per liter (mg/L) unless otherwise noted. Milligrams per liter are equivalent to parts per million.

## Reference

Vulcan Chemicals. Technical Data Sheet. Technical & Environmental Services. TDS 600-103. December 1998.

## Chlorine Dioxide Generators

### Introduction

Chlorine dioxide enjoys many different types of use particularly in water treatment. Among these are disinfection, bleaching, and chemical oxidation. The chlorine dioxide used in these applications is always generated on-site, usually from sodium chlorite, as an aqueous solution.

Chlorine dioxide is a reactive oxidizing gas that is readily soluble in water. Even dilute solutions (10 ppm) of chlorine dioxide have a characteristic yellow color. The maximum chlorine dioxide concentration typically produced in commercial generators is approximately 4000 ppm. This is to minimize the concentration of chlorine dioxide gas in equilibrium with the solution. Gas phase chlorine dioxide concentrations in excess of 10%, like ozone, can decompose explosively. This is the reason that chlorine dioxide must be generated at its point-of-use. This document will cover the chemistry of chlorine dioxide generation, generator design and operation requirements, generator safety requirements, features of many chlorine dioxide generators presently available in the market.

### Generation Chemistry

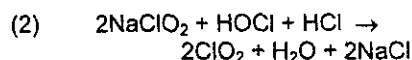
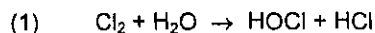
While chlorine dioxide may be produced from sodium chlorate ( $\text{NaClO}_3$ ), most small-scale generators use sodium chlorite ( $\text{NaClO}_2$ ) as their precursor chemical. The economic breakpoint between chlorite and chlorate generation is on the order of tons/day of chlorine dioxide. Three feed chemical combinations will be covered:

- 1) chlorine-sodium chlorite,
- 2) acid-sodium hypochlorite-sodium chlorite, and
- 3) acid-sodium chlorite.

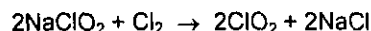
### Chlorine-Chlorite

This method, the most flexible and efficient method of generating chlorine dioxide, generates chlorine dioxide in a two step process. First, (equation 1), chlorine reacts with water to form hypochlorous acid ( $\text{HOCl}$ ) and hydrochloric acid ( $\text{HCl}$ ). These acids then react (equation 2) with sodium chlorite to form chlorine dioxide, water, and sodium chloride ( $\text{NaCl}$ ). The ratios of sodium chlorite and hypochlorous acid (chlorine) must be carefully controlled. Insufficient chlorine feed will result in a large amount of unreacted chlorite. Excess chlorine feed will result in the formation of sodium chlorate ( $\text{NaClO}_3$ ), which is the oxidation

product of chlorine dioxide. The typical operating conditions and yields for this method of generation are shown in Table 1.

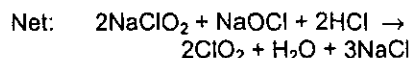
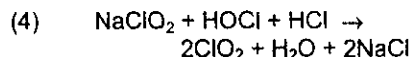


Net:



### Acid-Hypochlorite-Chlorite

This is an alternative to chlorine-chlorite generation that is used when chlorine gas is not available. First (equation 3), sodium hypochlorite is combined with hydrochloric or other acid to form hypochlorous acid. Sodium chlorite is then added to this reaction mixture to produce chlorine dioxide (equation 4).

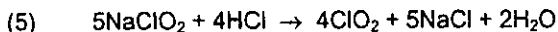


Since equations 2 and 4 are identical, the chlorine dioxide generation step is the same. Consequently, the typical operating conditions, yield, and purity for this method of generation are the same as for chlorine-chlorite generation. This method also shares the requirement of carefully balancing sodium chlorite and hypochlorous acid feeds, which is made more difficult by poor storage characteristics (rapid degradation) of sodium hypochlorite solutions. The typical operating conditions, and yields for this method of generation are shown in Table 1.

| Table 1                               |         |         |
|---------------------------------------|---------|---------|
|                                       | Minimum | Maximum |
| $\text{NaClO}_2$ (ppm)                | 1,340   | 5,360   |
| $\text{HOCl}$ (ppm as $\text{Cl}_2$ ) | 526     | 2,100   |
| pH                                    | 2.7     | 3.2     |
| $\text{ClO}_2$ , theory (ppm)         | 1,000   | 4,000   |
| $\text{ClO}_2$ , actual (ppm)         | 950     | 3,800   |

### Acid-Chlorite

Acid-chlorite is the simplest and easiest to operate generation chemistry. This is a consequence of the use of only two feeds and its simple reaction chemistry (equation 5). Instead of having to balance the amounts of sodium chlorite and hypochlorous acid, one merely has to provide sufficient hydrochloric acid. Excess acid does form undesirable reaction products. Unfortunately, there is no such thing as a "free lunch." This ease of operation comes at the cost of chlorine dioxide yield. The theoretical conversion of sodium chlorite to chlorine dioxide is only 80%, while the chlorine-chlorite and acid-hypochlorite-chlorite reactions both have theoretical conversions of 100%.



### Generator Design

Chlorine dioxide generators must feed and mix precursor chemicals and provide sufficient residence time for the generation reaction to go to completion. The required residence time varies from less than a minute for hypochlorous ( $\text{Cl}_2$  or  $\text{HCl-NaOCl}$ ) generation to 15 minutes for acid generation. Generators differ predominantly in the type of chemical feed systems they employ. Three types of designs are used: 1) vacuum feed systems, which pull fluids into the generator; 2) pressure feed systems, which push fluids into the generator; and 3) a combination of pressure and vacuum feed systems. While liquid chemicals (acid, sodium hypochlorite, and sodium chlorite solutions) can use any type of feed system, chlorine gas must be added by a vacuum (or combination) feed system.

### Vacuum Feed Systems

A vacuum feed system is composed of a venturi and a rotameter. The venturi or eductor uses the flow of a fluid (water) to create the vacuum that pulls the precursor into the generator. The venturi cross-section shown in the figure below demonstrates how this vacuum is created.

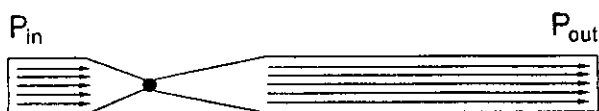
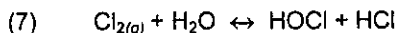


Figure 1 - Venturi

As water flows through the venturi, it passes through a narrow section where the increase in the water's velocity causes a vacuum. The amount of the vacuum formed depends upon the pressure drop ( $\Delta P$ ) across the venturi (the greater the pressure drop, the greater vacuum).

$$(6) \quad \Delta P = P_{in} - P_{out}$$

The conditions required for proper venturi function define the limit of this type of feed system. First of all, those applications that have a low supply water pressure ( $P_{in}$ ) or a high system back-pressure ( $P_{out}$ ), will require a booster pump to provide a large enough  $\Delta P$ . Second, the venturi feed system places a limit on the chlorine concentration that can be fed. As more and more chlorine is dissolved in water, the water pH decreases until it shifts the equilibrium (equation 7) to release chlorine gas. The pressure of this gas will prevent the venturi from operating. This occurs at chlorine concentrations around 4,000 ppm.



The feed rate of the precursor chemicals are measured and controlled by rotameters (see figure below). The amount of chemical fed is controlled by a needle valve and measured by a ball supported by the flowing chemical.

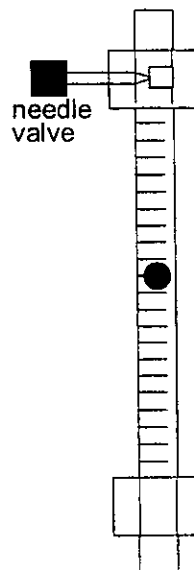


Figure 2 - Rotameter

The venturi may be installed before, after, or at the point of chemical mixing and reaction. Vacuum feed systems use venturi locations both at or after the mixing and reaction zone. Locating the venturi after the mixing and reaction zone mixes undiluted feed chemicals. This causes a very rapid reaction to form chlorine dioxide, but may also cause plugging of the mixing and reaction zone with sodium chlorite. Locating the venturi at the mixing and reaction site mixes and dilutes the feed chemical in the motive venturi water. This slows the reaction that forms chlorine dioxide but avoids plugging with sodium chloride. A venturi location before the mixing and reaction zone is typically used in combined feed systems to provide time for the hydrolysis of chlorine to form hypochlorous acid.

### Pressure Feed System

Pressure feed systems use chemical dosing pumps to push the precursor chemicals into the reaction chamber. Usually diaphragm positive displacement pumps are used (see figure below). A piston moves the diaphragm into (to the left) and out of (to the right) the pump head. During the outward piston stroke, solution is pulled into the pump head through the inlet check valve. During the inward piston stroke, solution is pushed out of the pump head through the outlet check valve and into the reaction chamber. The amount of chemical fed is controlled by the stroke length and stroke frequency. This type of feed system, while the most accurate, can be used only with liquid feed chemicals, such as used in acid-chlorite and in acid-hypochlorite-chlorite feed systems.

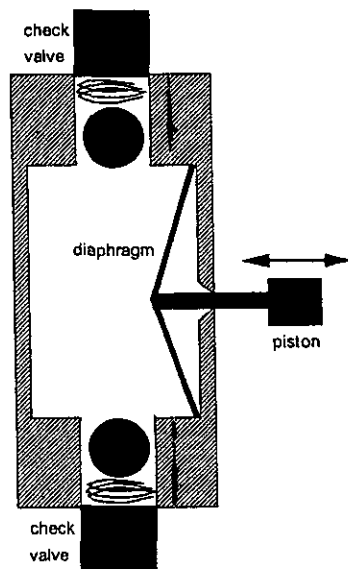


Figure 3 - Diaphragm Pump

### Combination Feed Systems

Combination feed systems are used only in chlorine-chlorite generators. The chlorine feed rate is controlled by a venturi and rotameter. The sodium chlorite feed rate is controlled by a chemical dosing pump.

### Safety Requirements

Numerous types of interlocks are usually built into chlorine dioxide generators. These serve two purposes: first, they prevent hazardous reaction conditions in the generator; and second, they ensure that only chlorine dioxide is being applied by shutting the system down when a precursor chemical is absent.

### Hazardous Conditions

Hazardous reaction conditions are the result of too high a concentration of chlorine dioxide in solution. If a gas phase forms above this solution, the chlorine dioxide in this gas phase can reach a level (10% v/v) where spontaneous, explosive decomposition can occur. Even if a gas phase can not form, decomposition can occur in solution from the "red complex,"  $\text{Cl}_2\text{O}_4$ , a species that can form in very concentrated solutions of chlorine dioxide and sodium chlorite. Its decomposition releases oxygen gas, which causes pressure increases. Consequently, it is critical to keep the chlorine dioxide in solution diluted with water. The minimum safety requirements are to 1) design the reaction chamber so that a gas phase can not form, and 2) provide a flow switch (safety interlock) that shuts the generator off in the event of loss of dilution water flow.

### Out of Chemical

To ensure the application of only chlorine dioxide, many generators incorporate "out of chemical" sensors that shut the generator down when a feed chemical is absent. These may be level switches in tanks, vacuum-pressure sensors for gas cylinders, or liquid displacement devices for pumps.

### Generator Automation

Chlorine dioxide generators are automated to provide modulation of chlorine dioxide feed rates based upon changes in flow (flow paced control) and chlorine dioxide demand of the water being treated (residual control). Theoretically, the chlorine dioxide feed rate may be varied by either modulating the precursor chemical feed rates to the generator or by turning the generator on and off. In practice, only pressure feed system generators can inexpensively modulate precursor chemical feed rates. Vacuum and combination systems are limited by the hydraulic requirements of their venturi and the optimum reaction conditions (concentration) for chlorine dioxide generation. Consequently, to achieve automatic operation, manufacturers of vacuum or combination feed system generators use a batch tank with a level switch to turn the generator on and off. A chemical dosing pump is used to feed chlorine dioxide solution. This allows the generator to operate at the optimum reaction conditions for good chlorine dioxide yield and purity.



**Further Information**

More detailed information on sodium chlorite is available on request through the Vulcan Chemicals Technical Service Department.

Call or write the Technical Service Department, Vulcan Chemicals, P.O. Box 385015, Birmingham, Alabama 35238-5015, 800/873-4898

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